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"Silicon Nano-Tips And Related Nano-Systems Involving Fluid And Carrier Transport For Miniaturized Spacecraft Power And Sensing Applications"

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Abstract

Ionic liquid ions sources (ILIS) extract ions from room temperature molten salts, or ionic liquids. Ion extraction is achieved by stressing the ionic liquid into a Taylor cone structure, formed on the apex of micro-sized, nanostructured tips known as emitters. These ion sources can be used in applications such as ILIS electrospray propulsion for multi-scale spacecraft and materials processing at the nanoscale. Through this research, the two fundamental life-limiting issues of ILIS operation have been identified and mitigated: electrochemical degradation and gas discharges. A distal electrode configuration was proposed and verified as a strategy to curtail electrochemistry. Furthermore, it was determined that trapped micro-bubbles of gas inside porous ILIS substrates can cause degassing during operation, leading to electrical discharges that provoke to device failure. It was demonstrated that discharges are suppressed through adequate liquid filling strategies. Lastly, novel fabrication techniques for emitter substrates and electrodes based on nanomaterials have been explored. Fabrication of porous dielectric substrates in micron-sized molds has been achieved by sintering of glass micro beads. In addition to strong student support (several graduate-level theses) and works published in the open literature, this research has facilitated continued collaboration with AFRL, AFOSR and other DoD agencies.

Introduction

Ionic liquid ion sources (ILIS) extract and accelerate molecular ions from micro-tip emitters wetted with room temperature molten salts (ionic liquids), for applications ranging from nanofabrication to space propulsion. Over the course of this grant, we have identified key operational limitations together with mitigation strategies. Two life-limiting mechanisms of ILIS have been addressed: electrochemical deterioration of the ionic liquid and emitter electrode, and carbonization of the ionic liquid due to electrical discharges. Furthermore, novel substrates and emitter fabrication techniques have been studied over the course of this research. The state of the problem, experiments and findings in each of these three research areas (electrochemistry, discharges, and emitter fabrication) are presented below. The discoveries realized during the period of performance are enabling the long-lifetime operation of ILIS devices and are already being implemented in ILIS technology.

Electrochemistry.
When a single ion polarity is extracted, counterions left behind accumulate over the electrode surface, producing a double layer (DL) of charge. Eventually, the electric potential across the DL becomes equal to the electrochemical window limit V_w of the ionic liquid, generating electrochemical reactions, which severely limit the lifetime in ILIS technology. To avoid charging to the limit, periodic voltage alternation is used, but this strategy is insufficient in high throughput applications. Previous models and experiments have overlooked the coupling between initial transient DL dynamics and charge diffusion in the cases of high emitter current. Thus, the dynamics of DL formation are revised and distal electrode contacts are introduced as the key to resolve detrimental electrochemical decomposition effects at the most critical location, namely the emitter tips.

In the distal contact approach, the voltage is applied to the liquid exclusively with an upstream electrode, with the emitter left floating electrically, as opposed to a direct contact where the voltage is applied directly to the emitter (see Figure 1). By having the emitter potential follow the ionic liquid potential, operation of ILIS could be achieved for an extended period of time with no apparent degradation of the emitter, as electrochemistry should be isolated to the upstream distal electrode. We perform two sets of experiments with this configuration to validate its effectiveness in mitigating electrochemistry. These high-impact results have been published in Applied Physics Letters.

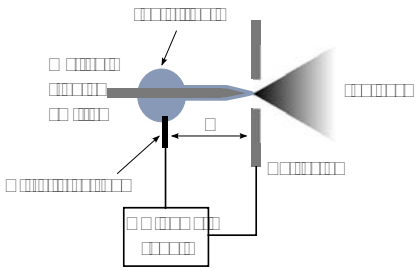

Figure 1. Distal electrode configuration

Electrochemistry experiments

In the first experiment, we test the feasibility of implementing distal electrode contacts with metal emitters by measuring the voltage drop across the liquid path. Two possible distal contact configurations are of interest: one in which the emitters are fabricated from an insulating material and another that uses emitters fabricated on metals, but separated from the distal electrode by a liquid layer. In the former configuration, there is no electrochemistry at the emitter surface because the local surface potential would simply follow the potential of the liquid. However, in the latter case the electric potential of the metal emitter substrate would be constant, while the potential difference across the DL

would change as a result of the ohmic drop along the liquid path from the back surface to the emitter tip, given by $\Delta V = IL/KA$ (I the current, L the liquid path length, K liquid conductivity, and A the effective cross-sectional area through which the current is transported). As long as ΔV is less than V_w, reactions will not occur at significant rates along the liquid path.

Given the relevance of this approach to the common practice of using metallic emitters, the potential drop along an externally wetted sharpened tungsten emitter 0.5 mm in DIA was measured with the setup shown in Figure 2(a). The emitter was wetted with the liquid EMI-BF_4 (1-ethyl-3-methylimidazolium tetrafluoroborate) and passed through a stainless steel cylindrical reservoir; this cylinder serves as the distal electrode. The exposed emitter length (and effective liquid path), L, was varied between 2 and 4 mm *in situ*. A square-wave voltage (+/-1285 V) was applied to the extractor at a frequency of 0.1 Hz. The emitter voltage with respect to ground is monitored using a high impedance electrometer. The current to the cylinder was monitored by a second electrometer and varied from 60 to 70 nA for short and long L, respectively. A sample of the voltage for two exposed lengths is plotted in Figure 2(b).

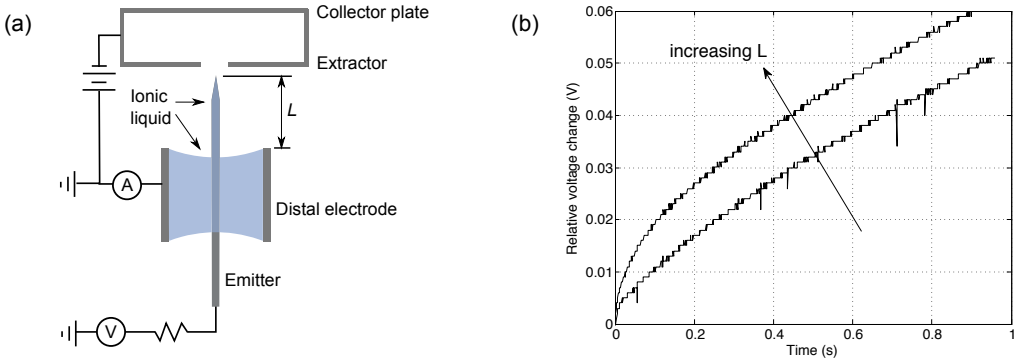

Figure 2. (a) Experimental setup for measurement of voltage drop along emitter implemented with distal contact (b) Results of charging experimetns with varying exposed length L

Eventually, the charging rates of the emitter in both cases become very similar and are consistent with uniform capacitive charging of the cylinder's inner surface (~0.04 V/s). The voltage offset between the two curves is due to a quick difference of initial slopes. Its value (~0.01 V) is also consistent with the ohmic drop (higher, for longer L) along the liquid layer of the exposed surface. Given the low value of the ohmic drop compared to the electrochemical window limit, it is unlikely that reactions will happen on the surface of the emitter.

On the second experiment, we compare the performance of emitters implemented with both distal and direct configurations. Two tungsten emitters wetted with the ionic liquid EMI-BF_4 were fired simultaneously, one with a Pt (92%) – W (8%) wire in distal contact with the liquid and the other with the traditional direct contact to the emitter. Both emitters were operated in positive DC mode for a total of 76 h, each with an average emitted current of 300 nA. The pressure in these experiments was below 5×10^{-7} Torr.

The emitters were visually inspected at the end of each run. As expected, the remaining liquid of both emitters appeared discolored from electrochemical reactions in which BF_4^-

ions are faradically discharged to the contact electrode. SEM images of the emitters pre- and post-test are shown in Fig. 3. In the distal contact configuration, the emitter appears intact whereas the directly contacted emitter shows clear signs of degradation. In particular, it is seen that tungsten at the apex was electrochemically etched away with noticeable material loss. Etching continued upstream as evidenced by a significant change in surface texture.

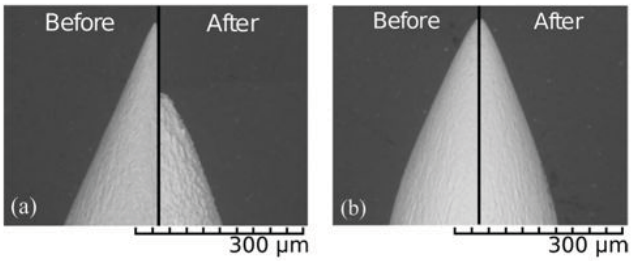

Figure 3. Tungsten emitters before and after firing. Tip etching and surface roughening is evident on the direct contact emitter (a); the distal contact emitter (b) appears undamaged.

Based on these findings, distal electrodes will be implemented in subsequent single emitter and emitter array configurations in combination with voltage alternation to avoid electrochemical deterioration.

Electrical Discharges

A second life-limiting mechanism arises when the ionic liquid is heated to temperatures on the order of 1000 K as a result of electronic discharge during operation. At these temperatures, the liquid can carbonize, producing solid deposits on the emitters and extractor that obstruct liquid flow and lead to device failure. Solid black carbonaceous structures have been observed on and around single porous emitters and emitter arrays after testing (see Figure 4), which were previously thought to be a consequence of electrochemistry or ablation. We hypothesized that air, trapped in the porous emitter material when filled with ionic liquid at atmospheric conditions, was being released as the pressure in the vacuum chamber was decreased and an electric field was applied. Under these conditions, regions of higher pressure could lead to electrical discharges that heat the liquid to its carbonization temperature. Upon further investigation, it was found not only that trapped gas in the emitters causes discharges, but also that inadequate liquid containment in the emitters can lead to failure.

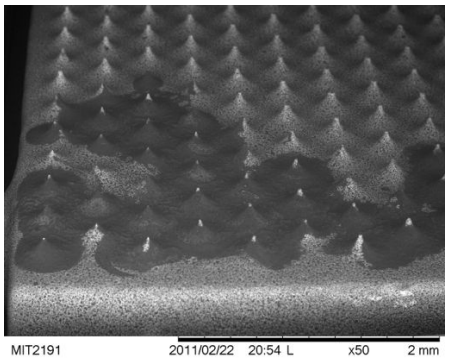

Figure 4. Ni emitter chip with evidence of carbon deposits due to propellant heating, a consequence of discharges

Discharge experiments

As a preliminary test for the hypothesis, two blunt porous nickel emitter tips wetted with EMI-BF_4 were fired, one filled at atmosphere and one filled in vacuum. The emitter filled in vacuum was fired without any intermediate atmospheric exposure. 1-2 kV were supplied to the emitters and the emitted current ranged from 0.2 to 1 µA. The tests were recorded using an optical microscope and a camera (30 fps).

During firing of the air-filled emitter, gas bubbles, discharges, and carbonization of the ionic liquid from the emitter were observed. Despite the difficulty capturing discharges with a low frame rate camera, a spark discharge was observed, pictured in Fig. 5(a). SEM images of the emitter pre and post-firing are shown in Fig. 5(b), showing clearly the carbon deposits formed due to the discharges. Emission from the vacuum-filled emitter was stable for 2 hours and none of the phenomena mentioned above were observed. SEM inspection of the emitter reveals it is clear of solid deposits after the test (Fig. 5(c)). The contrast between these results suggests that gas released from the porous substrate or the ionic liquid produces a region of significantly higher pressure between the electrodes, leading to discharges, as seen in the first test.

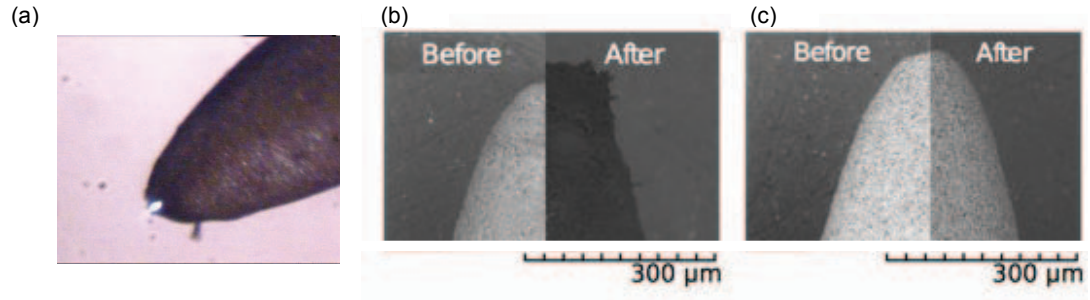

Figure 5. (a) Spark discharge captured during tests of a porous nickel emitter with EMI-BF_4, filled in atmospheric conditions (b) Same emitter before and after firing (c) Vacuum-filled emitter appears unchanged. The darker appearance in the image is due to a microscope setting.

We followed this experiment with a series of systematic tests using porous single emitters monitored by a suite of diagnostic instruments in order to verify the primary causes of discharges. The main hypothesis tested is if electrical discharges that present in porous ILIS are due to release of gas and/or subsequent expulsion of liquid that result from filling of porous substrates in gaseous atmospheres or the evaporation of water vapor or other contaminants from the environment. Several parameters were varied between tests, namely (1) filling condition (emitters filled in vacuum vs. emitters filled at atmospheric pressure in air, CO_2, Ar and N_2), (2) emitter material (nickel, tungsten or glass), and (3) emitter polarity (positive or negative emission). The emitters were fired while monitoring the emitter current and applied voltage and inspecting the emitters with a microscope. To detect the discharges accurately, an electromagnetic pulse detection antenna was installed in the test chamber. The vacuum chamber pressure is tracked with a hot cathode ionization gauge and the partial pressure of different gases present in the chamber is measured with a residual gas analyzer. Post-test SEM imaging is performed to determine the state of the emitter post firing.

The results of the tests are summarized in Table 1; the primary result obtained was whether discharges were present or not during firing. The polarity, not included in Table 1, did not affect the outcome at all. Emitters filled in gas atmospheres nearly always led to electrical discharges, which is in line with the hypothesis. Discharges that presented during tests in which emitters were filled in vacuum, however, were unexpected according to the hypothesis. Filling in vacuum improves the outcome, but does not prevent discharges. This technique inhibits both residual gas from filling and water vapor from the environment, and therefore should have precluded discharges. That discharges still occurred indicates another factor is at play. If the tests are separated by the degree of containment, i.e., whether or not the liquid is adequately distributed within the pores, it can be seen that the tests with inadequate liquid containment always present discharges

(Table 2). Inadequate containment can be identified by the occurrence of a large excess drop of liquid along the emitter (Figure 6), which effectively increases the backpressure compared to the case where the liquid is fully contained with the pores. This backpressure affects the balance between the applied electric, the surface tension, and the hydraulic impedance, and can lead to flooding and expulsion. Filling in vacuum without a large liquid pool at the upstream pore entrances was the only successful method of preventing discharges.

Table 1. Binary Discharge results for different values of variables tested.

	No discharges	Discharges present	Total Tests
Gas	**2**	**20**	**22**
Air	1	8	9
Glass		5	5
Ni	1	2	3
W		1	1
Ar		4	4
Ni		4	4
CO_2	1	8	8
Ni	1	8	9
Vacuum	**4**	**5**	**9**
Glass		4	
Ni	1		
W	3	1	
Grand Total	**6**	**25**	**31**

Table 2. Binary discharge results, reordered against containment variable.

	No discharges	Discharges present	Total Tests
Gas	**2**	**20**	**22**
Adequate containment	2	14	
Inadequate containment		6	
Vacuum	**4**	**5**	**9**
Adequate containment	4		4
Inadequate containment		5	5

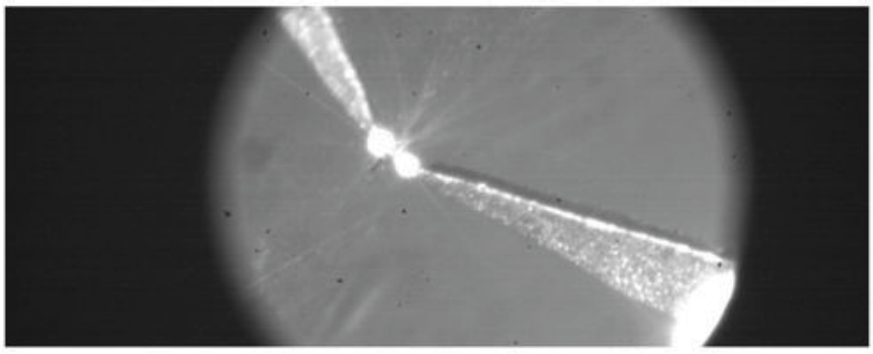

Figure 6. Optical microscope image of porous tungsten test emitter and its reflection on the metallic extractor. The emitter was filled with ionic liquid under vacuum and had a large upstream liquid pool. The frame clearly captures the occurrence of a discharge.

Substrate Materials and Fabrication

During the course of this grant we aimed to understand the role that materials at the emitter-vacuum interface play on the effectiveness of transporting flow and producing high ion beam currents in electrospray thrusters. Our initial research goals in this area were driven by two questions: first, how to scale thrust upwards by taking advantage of nano-structured ion emitters, which promote wetting of the propellant, and second, how to provide materials which guarantee a benign operational environment (particularly electrochemical, but also free from discharges and other issues). In this context, we investigated the fabrication of silicon nanotips and different treatments that could be used to manage the wetting of the ionic liquid on these structures, while preventing reactions. Furthermore, we considered techniques for electroplating nickel and platinum in emitter materials, as well as methods for electroforming emitter structures. When the distal electrode configuration was introduced, dielectric materials started to be considered as emitter substrates, and we have developed techniques for the fabrication of porous glass emitters from the sintering of micro beads.

Substrate Experiments

Silicon emitter arrays (shown in Fig. 7) were fabricated using standard photolithography with a combination of wet and dry etching. We studied several possible surface modifications for silicon with the goal of identifying appropriate strategies for the ionic liquid management on silicon emitter structures. The wetting behavior of the liquids EMI-BF_4 and EMI-Im (1-ethyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)amide) on chemically and/or structurally modified silicon surfaces was characterized through contact angle measurements. The surfaces studied included bare Si and combinations of 10 μm x 10 μm x 10 μm posts, nanograss, and octatridecyltrichlorosilane (OTS). Results showed that hydrophobic and hydrophilic behavior could be achieved for both liquids (see Figure 8 and Table 3); thus, we have developed possible strategies for treating silicon arrays to achieve the desired performance.

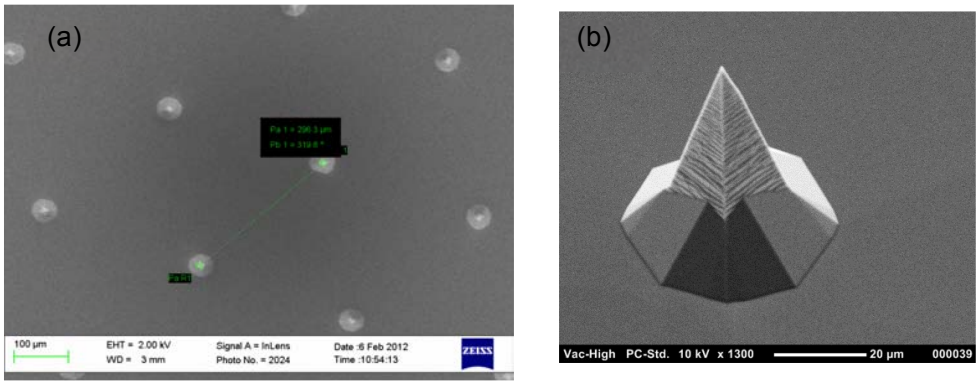

Figure 7. (a) SEM images of emitter tips: pitch is 300 um. (b) 45 degree view of emitter

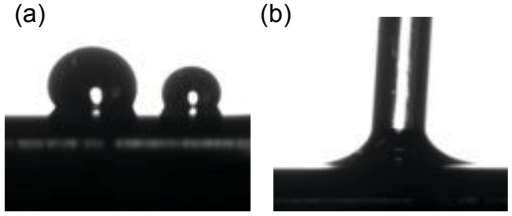

Figure 8. EMI-BF_4 drops on silicon surfaces, (a) silicon covered in nanograss and treated with OTS, and (b) silicon covered with nanograss, untreated.

Table 3. Contact angles of ionic liquids on silicon surfaces

Liquid	Structure	Treatment	Advancing / receding contact angle [deg]
EMI-BF_4	Bare silicon	none	25 ± 1
	Microposts	none	20±2/0
	Nanograss	OTS	137±2
	Nanograss	none	0
BMI-I	Bare silicon	none	34±2/9±2
	Microposts	none	0

‘

Another technique that was explored for the functionalization of emitters was electroplating. We performed two experiments, first, the electroplating of Ni onto silicon tips, and second, the electroplating of platinum onto nickel substrates. Porous nickel arrays had been electrochemically etched and tested successfully prior to this research, showing outstanding emission characteristics. Therefore, it was desirable to explore the possibility of plating nickel on silicon nanotips to alter wetting properties and improve its chemical stability. Electrochemical degradation of nickel substrates can be curtailed by covering the nickel with a layer of an inert metal such as platinum, which can be achieved by electroplating.

For electroplating, an anode and cathode (the article to be plated) are placed in an electrolyte bath along with a reference electrode. (see Fig. 9(a)). Current flows to the anode forming metal cations that associate with the anions in the solution. The electric field causes the cations to flow toward the cathode where they are reduced to zero valence state and deposited on the cathode.

Electroplating of Ni onto Si arrays was performed, as shown in Figure 9(b). A silicon array sample (such as one from Fig. 7) was placed in a nickel electrolyte bath (composed of nickel sulfamate, nickel chloride, and boric acid solution). 0.2 V were applied (vs. reference electrode) to the working electrode for 5 minutes, while maintaining the temperature at 50 C and mechanically stirring the solution. As seen in the image, a thin layer of nickel was deposited without need for a seed layer. Deposition favored corners and tips of emitters, suggesting the reactions occurred in the Faradaic regime.

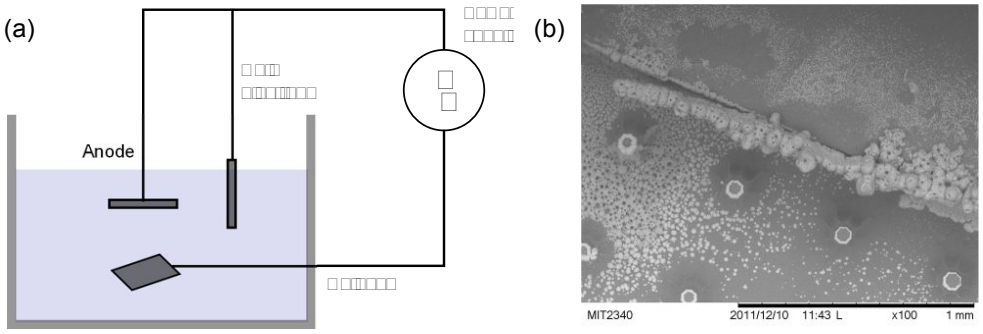

Figure 9. (a) Electrodeposition basic setup. (b) SEM image of microfabricated Si array showing some nickel deposition favoring sharp features

Using a similar setup (see Fig. 10(a)), preliminary platinum electroplating on solid and porous nickel substrates were performed. The samples were placed in a platinum

electrolyte bath ($H_2Pt(NO_2)_2SO_4$). The platinum anode motion could be controlled by a motorized station. Our preliminary results show that some platinum deposition occurred on porous nickel samples, although this technique needs to be improved for uniform deposition on the substrates (see Fig. 10(b)). Platinum appears to have been deposited on the corners of solid nickel samples, but a precipitate film may have formed on the surface, passivating it and preventing further cathodic reaction from taking place.

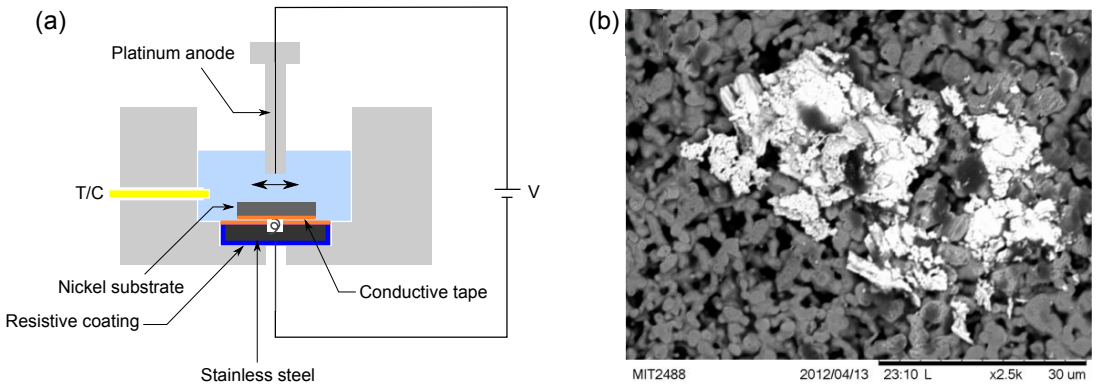

Figure 10. (a) Electroplating setup for platinum deposition. (b) Porous nickel substrate showing some platinum deposition after applying 0.1 V for 180 s.

Our results with electrodeposition motivated the use of electroforming for emitter arrays. It is desirable to use a bottom-up approach to fabricate emitters, offering greater control over pore size and a wider selection of materials. An experiment was conducted to evaluate the concept of electroforming emitters from nickel deposited onto a porous nickel substrate. A porous nickel sample was covered with a dry film photoresist mask, patterned, and placed in an electrolyte bath as in Fig 9(a). The solution consisted of nickel sulfamate, nickel chloride and boric acid. A potential of 0.3 V was applied to the working electrode for 20 minutes, with mechanical stirring and the temperature set to 50 C. The result of this process is shown in Figure 11. The dry film photoresist mask withstood the acidic plating solution, and more than 65 µm of nickel were deposited in exposed areas. This technique can be refined with higher resolution lithography techniques such as e-beam or interference lithograpy in order to achieve high density of emitters on a substrate.

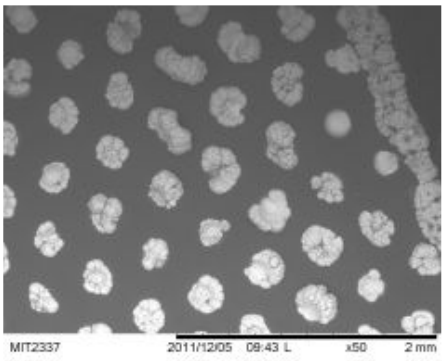

Figure 11. SEM photograph of Ni deposition results

Finally, porous glass fabricated from the sintering of glass microspheres has been developed and tested as an emitter substrate during this research. Pillar structures several tens of µm in diameter were made by depositing and sintering soda lime glass beads of about 4 µm diameter in a micro patterned silicon mold. The fabrication process for these pillars is as follows: first, a silicon mold is fabricated from a SOI wafer (Fig. 12(a)). The device and the handle layer were both patterned using standard photolithography techniques and DRIE, with a slight overetch in the handle layer that

should result in an extra porous region around the porous emitter. The buried oxide layer is then etched. (Fig. 12 (b)-(d)). The beads are introduced in a water suspension to the device with the aid of an ultrasound bath. (Fig. 12(e)). The mold then undergoes a carefully designed thermal cycle to ensure the cohesion of the soda lime beads (Fig. 12(f)), and the device layer is finally removed using a highly selective XeF_2 etch (Fig. 12(g); note the handle layer has a protective photoresist layer that is removed in the last step, Fig. 12(h)). A sample pillar structure is shown in Fig. 12(i). While these pillars are still not fully shaped into an emitter structure, we have validated the sintering approach and the possibility of using this technique to create emitter arrays.

To study the electrospray capabilities of the porous glass, a piece of porous glass from the handle layer of the chip was removed from the silicon chip and mechanically sharpened into an emitter structure. The emitter was fired using a triangular voltage signal with amplitude of +/-2.5 kV, and current levels of up to 6 µA were emitted by this single tip. This demonstrates that porous glass tips could be used to increase the emitter current and hence improve the throughput of ILIS devices.

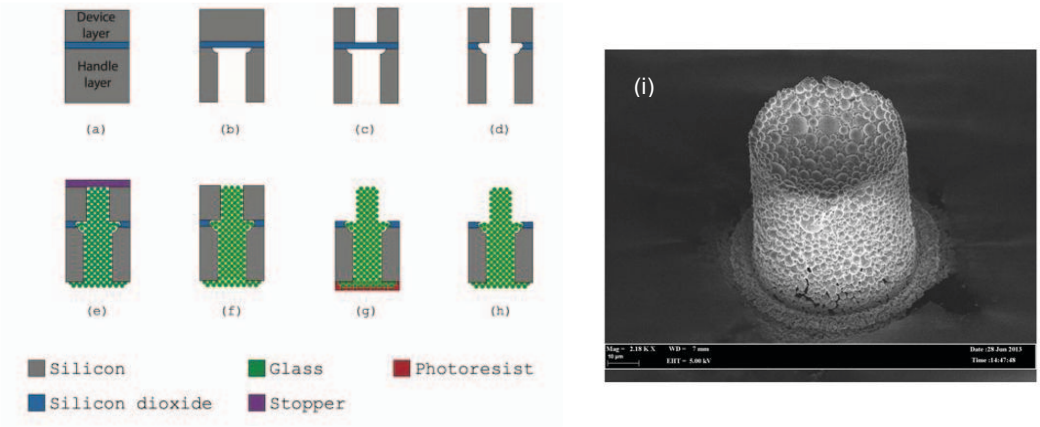

Figure 12. (a)-(h) Fabrication process for porous emitters for electrospray embedded in silicon substrate and made of glass beads. (i) Single emitter having a height of 50 µm and a height of 60 µm made of sintered glass beads.

Results and Discussion

Crucial mitigation techniques for eliminating detrimental electrochemical reactions and carbonization effects due to electrical discharges have been developed thanks to this grant. Distal electrode contacts are now routinely implemented on all ILIS developed by our group, and we use the liquid filling protocols recommended by our recent findings to guarantee discharge-free operation. This technology has enabled prolonged tests on emitter arrays operating at high currents, which simply would not have been possible before. Additionally, it has enabled the use of dielectric materials as emitter substrates. The use of distal electrodes is also fundamental for the implementation of ILIS in applications such as focused ion beams, in which voltage alternation is cumbersome. Future work on distal contacts includes the development of high-surface area electrodes that may allow reducing the required alternation frequencies on high throughput applications. Although we have a basic understanding of how to prevent failure due to discharges, the dynamics of discharge processes are still not well understood, and a

careful theoretical study is required to understand precisely how emitter filling, geometry, and electrostatic conditions lead to discharge events.

Emitter substrate and fabrication techniques have also been extensively explored with this grant. Silicon and nickel emitter arrays have been fabricated, and preliminary wetting studies of ionic liquids on silicon showed that precise patterning could improve spatial control of propellants. A thin layer of Ni was electrodeposited on silicon demonstrating the feasibility of another surface treatment for improving wetting on this substrate. The concept of electroforming emitter arrays was investigated via an experiment in which structures 65 um tall and 200 um in diameter were formed by depositing Ni through a patterned mask.

The formation of porous substrates from the sintering soda lime microspheres has demonstrated that it is possible to form micro-structures with silicon molds, which should be a highly-repeatable and controllable technique. This technique needs to be improved to ensure the adequate uniformity of the porous substrate through better control of the micro glass bead sizes, and work into shaping porous pillars into complete emitter structures still needs to be performed. The sintering approach has a lot of potential for the densification of ILIS devices, as nanoscale beads are available and it should be possible to sinter these materials into nano-sized emitters.

One of the most relevant results of this research has been the validation of dielectric materials as substrates for the micro-tips, after introducing the distal electrodes. This has enabled the use of the methods described above, but perhaps the most interesting aspect are the future possibilities, including the use of nano-structured polymer and ceramic materials for this application. This avenue is currently being explored in the new AOARD work and we expect significant results in the near future.

List of Publications that result form your AOARD supported project

(1) N. Brikner and P.C. Lozano, The role of upstream distal electrodes in mitigating electrochemical degradation of ionic liquid ion sources, Appl. Phys. Lett. 101, 193504 (2012), doi:10.1063/1.4766239
(2) N. Brikner and P.C. Lozano, Electrostatic Phenomena in Ionic Liquid Ion Sources, in Proceedings of the 49th AIAA/ASME/SAE/ASEE Joint Propulsion Conference, San Jose, CA, July 2013
(3) J. Xie, M. D. Canonica, P.C. Lozano, Fabrication of Electrospray Thrusters by Sintering Glass Microspheres, in Proceedings of the 49th AIAA/ASME/SAE/ASEE Joint Propulsion Conference, San Jose, CA, July 2013
(4) J. Xie, MIT Department of Aeronautics and Astronautics M.S. Thesis, June 2014. Available on http://hdl.handle.net/1721.1/90809
(5) N. Brikner, MIT Department of Aeronautics and Astronautics Ph.D. Thesis, February 2015 (document will be available shortly)